* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a hard carbon film sliding member and the low friction hard carbon film sliding member especially used in lubricating oils, such as an engine oil and transmission oil.
[0002]
[Description of the Prior Art]A hard carbon coat is amorphous-like a carbon film or a hydrogenated carbon film, and is also called a-C:H (amorphous carbon or hydrogenation amorphous carbon), i-C (eye carbon), and DLC (diamond like carbon or Dee Elsie).
[0003]Vapor phase synthetic methods, such as plasma CVD method which carries out plasma decomposition of the hydrocarbon gas, and forms membranes, and an ion-beam-deposition method using carbon and a hydrocarbon ion, the ion plating method which evaporates graphite etc. by arc discharge and forms membranes, etc. are used for the formation.
[0004]A hard carbon coat is high hardness and has the low friction performance which was smooth, and the surface excelled [performance] in abrasion resistance, and was excellent in the low friction coefficient from the solid lubrication nature. And the coefficient of friction of a hard carbon film under-less lubricous is about 0.1 to the coefficients of friction on the usual smooth surface of steel materials being 0.5-1.0 under-less lubricous.
[0005]Now, taking advantage of these outstanding characteristics, application to working jigs, such as cutting tools including a drill edge and a grinding tool, a plastic-working public-funds type and a valve cock, the moving part under [like a capstan roller]-less lubricous, etc. is achieved.
[0006]Also in machine parts, such as an internal-combustion engine which slides in a lubricating oil, the demand of liking to reduce mechanical loss as much as possible from the field of energy expenditure or an environmental problem is increasing, and by the severe part

of the large sliding condition of friction loss especially. Low friction-ization by the hard carbon coat which has these solid lubrication nature is desired.

[0007]

[Problem(s) to be Solved by the Invention]However, when a moving part is coated with the conventional above-mentioned hard carbon film and it is made to slide in lubricating oils, such as engine oil and a transmission oil, become a certain amount of low friction from the smooth nature, but. The problem that only low friction performance equivalent to the slide member which carried out hard coat processing in which it did not have other solid lubrication nature, for example, the slide member which performed titanium nitride (TiN) and chromium nitride (CrN) ion plating coat processing, was shown became clear. That is, in the conventional slide member by which hard carbon coat processing was carried out, although there was solid lubrication nature under-less lubricous, the problem that only friction performance equivalent to the coat processing slide member which does not have the solid lubrication nature of equivalent surface roughness, or the steel part by which super-finishing processing was carried out was shown became clear.

[0008]For example, when three 3/8-inch balls are pushed by the load of 1kgf in a lubricating oil and it lets it slide in the relative velocity of 0.03 m/sec, the coefficients of friction of the diamond like carbon which is a hard carbon film are 0.10-0.12, In the steel material which does not carry out coat processing by equivalent surface roughness, or a chromium nitride (CrN) ion-plating-treatment film and a lubricating oil, it is an equivalent coefficient of friction.

[0009]Generally various extreme pressure additives are added by an engine oil and transmission oil for the purpose of wear-resistant improvement and the improvement in the friction characteristic, These additive agents are added targeting the effect of mainly reducing friction on the surface of the slide member made from steel metal and by generating the resultant of an additive agent on the sliding part surface by adsorption or sliding, or controlling contact of metal and improving abrasion resistance.

[0010]However, in the conventional hard carbon film sliding member processed by plasma CVD method etc. if it was in the lubricating oil containing such an additive agent. The surface was stable, it was hard to produce adsorption of an oil additive agent and additive agent reaction film formation compared with the surface of metal which does not give a coat, and it turned out that the performance which an additive agent has cannot fully be pulled out.

[0011]

[Objects of the Invention]It is that this invention is made paying attention to these problems, and the specific metal content in a carbon coat considers it as the slide member which processed the hard carbon coat which is 5 - 70at%, It aims at providing the slide member which the solid lubrication nature worked effectively and was excellent in abrasion resistance by low friction also in the lubricating oil.

[0012]
[Means for Solving the Problem]specific metallic element content [in / in order to attain the above-mentioned purpose, as a result of inquiring wholeheartedly / a hard carbon coat] -- 5 - 70at% -- the low friction performance in inside of a lubricating oil was made realizable by having had composition to include.
[0013]Although there is almost no report and it is the translation which had many questions about the friction characteristic of a hard carbon coat in inside of this lubricating oil, By this invention, it clarifies about influence which it has on the friction characteristic in inside of a lubricating oil of specific metallic element concentration contained in a hard carbon coat, and specific metallic element concentration of a hard carbon coat which can realize low friction in a lubricating oil is specified.
[0014]Namely, a hard carbon film sliding member concerning this invention, In a hard carbon film sliding member used in a lubricating oil as indicated to claim 1, at least -- a surface layer -- the [of a periodic table of the elements] -- at least one sort of metallic elements chosen from among IIb, III, IV, Va, VIa, VIIa, and a group VIII -- 5 - 70at% -- it is characterized by containing.
[0015]And in a hard carbon film sliding member concerning this invention, as indicated to claim 2, content of a metallic element shall be 25 - 60at% of a range.
[0016]Can consider it as the thing according to claim 3 as which said metallic element is chosen from among molybdenum (Mo), tungsten (W), niobium (Nb), titanium (Ti), and iron (Fe) like, and like a statement to claim 4, A hard carbon coat which constitutes a hard carbon film sliding member shall be a diamond like carbon film (amorphous carbon film) produced by sputtering, plasma CVD, or ion plating.
[0017]It can be considered as the thing according to claim 5 whose surface roughness thickness of a hard carbon coat is 0.5 micrometers or more 10 micrometers or less, and is less than Ra0.1micrometer like and whose surface hardness is 1000 or more Hv(s) further again.
[0018]Content of a metallic element is 25 - 60at% like a statement to claim 6 further again, Thickness of a hard carbon coat is 0.5 micrometers or more 10 micrometers or less, and surface roughness is less than Ra0.1micrometer, and surface hardness is 1000 or more Hv(s), A metallic element shall be molybdenum (Mo) and a hard carbon coat which constitutes a hard carbon film sliding member shall be a diamond like carbon film (amorphous carbon film) produced by ion plating.
[0019]A hard carbon film sliding member by this invention can be made into the thing according to claim 7 used for adjusting SIMM or a valve lifter of a valve gear of an internal-combustion engine like.
[0020]Further again a hard carbon film sliding member by this invention, being according to claim 8 -- using mineral oil and synthetic oil as base oil, and making 50-1000 ppm and

dithiophosphate zinc into a phosphorus pool by making molybdenum dithiocarbamate into the amount of molybdenum like, -- 0.01 - 0.2wt% -- being used in an included lubricating oil **** -- being according to claim 9 -- like, using mineral oil and synthetic oil as base oil -- sulfur (S) systems, such as sulfurized oil fat, polysulfide, and olefin sulfide, -- content of the sulfur (S) ingredient shall be used in a lubricating oil which is more than 0.2wt% including an additive agent

[0021]

[Function of the Invention]As for the hard carbon film sliding member concerning this invention, it is easy to form a resultant in the surface, an extreme pressure additive becomes being easy to stick by having had the above-mentioned composition to the surface, and it becomes possible to consider it as a low friction hard carbon film sliding member in a lubricating oil. For example, mineral oil and synthetic oil which are used for an engine oil etc. for the purpose of fuel efficiency are used as base oil, It is under [lubricating oil / which makes molybdenum dithiocarbamate the amount of molybdenum and contains 0.01 - 0.2wt% by making 50-1000 ppm and dithiophosphate zinc into a phosphorus pool] setting, Although the coefficient of friction was high rather than the steel slide members which the additive agent coat of molybdenum dithiocarbamate and dithiophosphate zinc added as an extreme pressure additive is not formed into a lubricating oil in the conventional hard carbon coat surface, and do not form the conventional carbon coat, the [of specific metal, i.e., a periodic table of the elements,] -- the coat of lubricating oil additive being formed in the surface, and at least one sort of metallic elements chosen from among IIb, III, IV, Va, VIa, VIIa, and a group VIII by making a 5-70at% carbon coat contain, A low coefficient of friction will be obtained.

[0022]And the low friction effect was not acquired as the specific metal content concentration of the hard carbon coat surface is less than [5at%], but 70at% was made into the maximum in order for the abrasion resistance under high planar pressure to run short, if it becomes an excess of 70at%.

[0023]The low friction characteristic in the inside of a lubricating oil will be obtained without making specific metallic element content into 25 - 60at% of the range spoiling abrasion resistance and smooth nature still more preferably. the metallic element added to a carbon coat -- the [periodic-table-of-the-elements] -- among IIb, III, IV, Va, VIa, VIIa, and a group VIII, When reaction coat formation of an additive agent is taken into consideration, it is preferred to be chosen out of among molybdenum (Mo), tungsten (W), niobium (Nb), titanium (Ti), and iron (Fe).

[0024]It is preferred to use less than Ra0.1micrometer in consideration of the low friction characteristic and the partner aggression about the surface roughness of a carbon coat, and, as for surface hardness, it is preferred to be referred to as 1000 or more Hv(s) which can secure abrasion resistance. As for thickness, since the remaining stress in a film may become

large and it may exfoliate automatically if it becomes a tendency which runs short of adhesion strength as it is less than 0.5 micrometer and becomes an excess of 10 micrometer about the thickness of a surface coat, it is preferred to consider it as the range of 0.5-10 micrometers.
[0025]
[Effect of the Invention]In the hard carbon film sliding member which is used in a lubricating oil according to the hard carbon film sliding member by this invention, at least -- a surface layer -- the [of a periodic table of the elements] -- at least one sort of metallic elements chosen from among IIb, III, IV, Va, VIa, VIIa, and a group VIII -- 5 - 70at%, since it shall contain, The remarkably outstanding effect of it being easy to form a resultant in the surface, and an extreme pressure additive becoming being easy to stick to a rear face, and becoming possible to consider it as a low friction hard carbon film sliding member in a lubricating oil is brought about.
[0026]And the remarkably outstanding effect of becoming possible to obtain the low friction characteristic in the inside of a lubricating oil is brought about, without spoiling abrasion resistance and smooth nature, when the content of a metallic element shall be 25 - 60at% of a range as indicated to claim 2.
[0027]And by choosing said metallic element from among molybdenum (Mo), tungsten (W), niobium (Nb), titanium (Ti), and iron (Fe) again, as indicated to claim 3, When reaction coat formation of an additive agent is taken into consideration, the remarkably outstanding effect that it may become effective is brought about.
[0028]As indicated to claim 4, further again, When the hard carbon coat which constitutes a hard carbon film sliding member shall be a diamond like carbon film (amorphous carbon film) produced by sputtering, plasma CVD, or ion plating, The remarkably outstanding effect that the surface is able to consider it as the hard carbon coat which has the low friction performance which was smooth, was excellent in abrasion resistance, and was excellent in the low friction coefficient with the solid lubrication performance which itself has with high hardness is brought about.
[0029]Further again by considering it as the thing according to claim 5 whose thickness of a hard carbon coat is 0.5 micrometers or more 10 micrometers or less like, It enables thickness for thickness to prevent the fall of the adhesion strength by a small thing, and to prevent increase of the remaining stress in the film by a large thing, Surface roughness by less than Ra0.1micrometer and when surface hardness shall be 1000 or more Hv(s), Surface roughness is enabled to prevent degradation of the low friction characteristic and the increase of the partner aggression by a large thing, and the remarkably outstanding effect that good abrasion resistance can be secured now by setting surface hardness to 1000 or more Hv(s) is brought about.
[0030]The content of a metallic element is 25 - 60at% like the statement to claim 6 further

again, The thickness of a hard carbon coat is 0.5 micrometers or more 10 micrometers or less, and surface roughness is less than Ra0.1micrometer, and surface hardness is 1000 or more Hv(s), When a metallic element shall be molybdenum (Mo) and the hard carbon coat which constitutes a hard carbon film sliding member shall be a diamond like carbon film (amorphous carbon film) produced by ion plating, The effect which becomes in work size that it is possible to provide the slide member which is low friction in lubricant and was further excellent by the sliding characteristic is brought about.

[0031]The remarkably outstanding effect of becoming possible to make the valve train characteristic of an internal-combustion engine much more good is brought about further again by [according to claim 7] using for the adjusting SIMM or the valve lifter of a valve gear of an internal-combustion engine like.

[0032]Mineral oil and synthetic oil are used as base oil like a statement further again at claim 8, making 50-1000 ppm and dithiophosphate zinc into a phosphorus pool by making molybdenum dithiocarbamate into the amount of molybdenum -- 0.01 - 0.2wt% -- by making as [use / in the included lubricating oil], The coat of lubricating oil additive is formed in the surface, and the remarkably outstanding effect of becoming possible to obtain a low coefficient of friction is brought about.

[0033]Mineral oil and synthetic oil are used as base oil like a statement further again at claim 9, sulfur (S) systems, such as sulfurized oil fat, polysulfide, and olefin sulfide, -- by making including an additive agent as [use / the content of the sulfur (S) ingredient / in the lubricating oil which is more than 0.2wt%], The remarkably outstanding effect of becoming possible to realize sufficiently good low friction performance in the inside of a lubricating oil is brought about.

[0034]

[Example]It cannot be overemphasized that this invention is not hereafter limited to the example shown below although an example explains this invention in detail.

[0035](Examples 1-7) The rubbing test was done with the specimen 10 which coated the hard carbon coat 12 on the with a [as shown in drawing 1 / 30 mm in diameter and 4 mm in thickness] disk substrate 11. The specimen 10 at this time should produce the hard carbon coat 12 on the disk substrate 11 by specification as shown in Table 1.

[0036]Example 1, coating a hard carbon coat with the plasma CVD method using hydrocarbon gas, after Ra0.04micrometer carries out super-finishing processing of the surface of the substrate 11 which consists of carburized steel (JIS SCN415). Mo element was added in the carbon coat so that the sputtering process which used Mo as the target material might be performed within the same vacuum housing and Mo concentration of the carbon coat surface might be 27at%. The coat surface was Ra0.09micrometer without finish-machining after membrane formation.

[0037]After Example 2 carries out super-finishing processing of the surface of the substrate 11 at Ra0.04micrometer, W is coated by the sputtering process which used W as the target material further after forming the diamond like carbon (DLC) coat 12 on the substrate 11 using hydrocarbon gas with a plasma CVD device, W element was added in the carbon coat so that W concentration of the hard carbon coat surface might be 48at% by repeating this by turns and considering it as a cascade screen.
[0038]Examples 3-6 used Fe of each addition metal, Ti, Cr, and W for the change of Mo target material of Example 1 as a target material, and they added the metallic element in the carbon coat so that the addition metal concentration of the carbon coat surface might serve as a value of Table 1 by the same method as Example 1. The concentration of each hard carbon coat was W10at% in Example 6 Cr30at% in Example 5 Ti25at% by Example 4 Fe30at% at Example 3. Each coat surface roughness was 0.07-0.08 micrometer of Ra without finish-machining after membrane formation.
[0039]After Ra0.04micrometer carries out super-finishing processing of the surface of the substrate 11 with which Example 7 consists of carburized steel (JIS SCN415), Coating a hard carbon coat by the ion plating method using graphite and molybdenum (Mo) as an evaporation source, Mo element was added in the carbon coat so that Mo might be coated within the same vacuum housing and Mo concentration of the carbon coat surface might be 40at%. Each coat surface roughness was Ra0.09micrometer without finish-machining after membrane formation.

[0040](Comparative examples 1-5) The time of having manufactured the slide member of the comparative example as shown in Table 1, The slide member which carried out the grinding process of the surface of the substrate 11 with which the comparative example 1 consists of carburized steel (JIS SCN415) to Ra0.24micrometer, The slide member by which the comparative example 2 coated the slide member of the comparative example 1 with the titanium nitride (TiN) coat of hardness Hv1500 which has 2.0-micrometer thickness by the ion plating method further, The comparative example 3 is the slide member which formed the diamond like carbon (DLC) coat 12 on the substrate 11 using hydrocarbon gas with the plasma CVD device, after Ra0.04micrometer carries out super-finishing processing of the surface of the substrate 11 which consists of carburized steel (JIS SCN415).
[0041]The slide member and the comparative example 5 which added W element to the hard carbon coat so that W concentration of the surface might be 2at% by the method as Example 6 that the comparative example 4 is the same are the slide member which added W element to the hard carbon coat so that W concentration of the surface might be 80at% by the same method as Example 6.
(Example of a rubbing test) The coefficient of friction was measured using the abrasion tester 20 of a pin one disk type as shown in drawing 2 (a) as a friction test device. This device is

arranged enabling free rotation of the work table 22 supported by the axis of rotation 21 enabling free rotation, Install the specimen slide member 23 in this work table 22, and outer diameter phi5mm and SUJ2 roller for roller bearing 5 mm in length are used for the upper surface side of this specimen slide member 23 as a pin, The pin 24 is arranged three pieces, as shown in drawing 2 (b), and it is constituted so that it may push by P:1.0 kg of load with the spring 25. At this time, the pin 24 is being fixed, respectively so that it cannot rotate in the electrode holder 24H. And the torque according to the frictional force which the axis of rotation 21 is connected with the motor 26, rotates with the relative sliding velocity of 0.01-1.0 m/sec to the ball pin 24, and generates between the pin 24 and the specimen slide member 23 shall be measured by the load cell 27, and the coefficient of friction shall be computed. The oil bath tub 28 shall be installed, and it shall be set up so that an oil temperature may be 80 ** by the oil-temperature control unit which is not illustrated, so that the specimen slide member 23 may be immersed into the lubricating oil 28L.

[0042]The slide member of each example and a comparative example is arranged as the specimen slide member 23 of the frictional testing machine 20 to Table 1, and the result of having measured the coefficient of friction in the lubricating oil is shown.

[0043]The test condition was performed with load load 15kgf (planar pressure 0.23GPa) to the three pins 24, and the sliding velocity of 0.03-1.0 m (30-1000 rpm)/sec. The engine oil aiming at the reducing friction in which a lubricating oil uses the usual engine oil and mineral oil as base oil, makes molybdenum dithiocarbamate the amount of molybdenum, and contains 0.12wt% by making 500 ppm and dithiophosphate zinc into a phosphorus pool, and -- using mineral oil as base oil -- the sulfur (S) system of polysulfide and olefin sulfide -- the sulfur (S) content in a lubricating oil used S system additive agent lubricating oil which is 0.5wt% including the additive agent.

[0044]

[Table 1]

区分	基材	皮膜処理	成膜法	金属およびその添加量 (at%)	膜厚 (μm)	硬度 (Hv)	表面粗さRa (μm)	摩擦係数 μ (0.5m/sec)		
								エンジンオイル	ジチオカーバメート添加剤含有油	いおう系添加剤含有油
実施例1	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	Mo 27at%	1.0	1300	0.05	0.081	0.058	—
実施例2	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	W 48at%	1.0	1150	0.09	0.079	0.039	0.078
実施例3	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	Fe 30at%	1.0	1300	0.07	0.095	0.043	0.081
実施例4	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	Ti 25at%	1.0	1200	0.07	0.091	0.055	—
実施例5	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	Cr 35at%	1.0	1300	0.08	0.095	0.061	0.085
実施例6	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	W 10at%	1.0	1400	0.08	0.090	0.060	0.087
実施例7	浸炭鋼	硬質炭素皮膜(DLC)	イオンプレーティング法	Mo 40at%	0.5	2300	0.09	0.071	0.038	0.077
比較例1	浸炭鋼	無し	—	—	—	—	0.09	0.106	0.038	—
比較例2	浸炭鋼	窒化チタン(TiN)	イオンプレーティング法	—	—	1500	0.04	0.104	0.096	—
比較例3	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	無し	1.0	1800	0.07	0.095	0.062	0.093
比較例4	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	W 2at%	1.0	1800	0.07	0.096	0.064	0.093
比較例5	浸炭鋼	硬質炭素皮膜(DLC)	プラズマCVD法	W 80at%	1.0	850	0.08	剥離	剥離	剥離

[0045]So that the measuring result of the coefficient of friction in sliding-velocity 0.5 m/s (500 rpm) shown in Table 1 and drawing 3, drawing 4, and drawing 5 may show, In the usual engine oil, rather than any of the comparative examples 1-5, the hard carbon coat of Examples 1-7 which added specific metal is low friction, and was considered to be an effect by an additive agent reaction coat being formed. In the examination in the engine oil which uses mineral oil as base oil, makes molybdenum dithiocarbamate the amount of molybdenum, and contains 0.12wt% by making 500 ppm and dithiophosphate zinc into a phosphorus pool. It compares with the slide member which coated the hard carbon coat of the comparative example 3 which does not add metal, By the hard carbon film sliding member of Examples 1-7 containing metal showing a low coefficient of friction, and the hard carbon film sliding member of Examples 2 and 7 being equivalent to the coefficient of friction of the comparative example 1, and making metal contain to a hard carbon coat, It was thought that a surface additive agent coat reaction equivalent to steel slide members came to arise.

[0046]On the other hand, if the comparative example 3 and metal addition which do not contain metal are in the hard carbon film sliding member below 5at%, or the slide member of the comparative example 2, Although an additive agent coat is generated by the mating material pin, since a coat was not generated on the surface of self, it turned out that the reduction effect of friction like the comparative example 1 or an example is not acquired.

[0047]moreover -- using mineral oil as base oil from comparison of Examples 2-7 and the comparative examples 3 and 4 -- the sulfur (S) system of polysulfide and olefin sulfide -- including an additive agent, even if the sulfur (S) content in a lubricating oil is in S system additive agent lubricating oil which is 0.5wt%, the same thing can say.

[0048](Example of a system examination) Even the cam at the time of using for adjusting SIMM 60 of the valve gear of an internal-combustion engine as shows drawing 6 the hard

carbon film sliding member of Examples 2 and 7 measured the friction loss torque of the hit. At this time, torque measurement was measured with the torque meter attached to the cam-shaft axis 52 which is not illustrated.

[0049]In the valve gear of the internal-combustion engine which shows drawing 6, a suction valve or the exhaust valve 53 is inserted in the valve guide 54, and the valve lifter 55 is installed above the axis end of the valve 53. The valve spring 57 is fixed to the valve 53 by the retainer 58 and the cotter 59 between the cylinder head 56 and the valve lifter 55, and load of the load by the spring 57 is carried out in the direction which closes the valve 53. As shown in a figure, adjusting SIMM 60 has fitted into the upper surface of the valve lifter 55 further again, and it is adjusted by the thickness of adjusting SIMM 60 so that clearance with the cam 51 may be set to about 0.3 mm. The cam-shaft axis 52 is driven via a timing belt by the drive of the crankshaft which is not illustrated. And when the cam-shaft axis 52 drives, the cam 51 rotates, and it ****s to adjusting SIMM 60, and has become a mechanism in which the valve 53 is made to move reciprocately. The test conditions at this time are the cam shaft number of rotations (this [idling tense]) of 300 rpm, spring Max load 50kgf, and 80 ** of engine oil temperature, The surface roughness of adjusting SIMM 60 and the partner cam 51 which slides should perform super-finishing processing, and Ra0.05micrometer shall be made to it.

[0050]The loss torque at the time of using for adjusting SIMM 60 similarly also measured the slide member of the comparative example 1 currently conventionally used for comparison, and the comparative example 3 which carried out hard carbon coat coating on the same conditions. The measured result is shown in drawing 5. At this time, the engine oil used the engine oil which makes molybdenum dithiocarbamate of the conventional engine-oil 5W-30SJ and W-30 5 about viscosity the amount of molybdenum, and contains 0.12wt% by making 500 ppm and dithiophosphate zinc into a phosphorus pool.

[0051]Like the pin disk rubbing test, compared with the comparative example, the adjusting SIMM of the example had small friction loss torque, and having excelled in the low friction performance was admitted so that the measuring result of the loss torque shown in drawing 7 might show. And especially Example 7 using the ion plating method became low friction torque also in which oil.

[Translation done.]